



Deoxygenation of methyl laurate as a model compound to hydrocarbons on transition metal phosphide catalysts

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ABSTRACT

A series of silica-supported metal (Ni, Co, Fe, Mo and W) phosphides were investigated for the deoxygenation of methyl laurate as a model compound to hydrocarbons. To insight into the mechanism, the deoxygenations of the intermediates (lauric acid, dodecanal and dodecanol) were also evaluated. For comparison, Ni/SiO₂ and PO_x/SiO₂ were also studied. At 573 K, 2.0 MPa and methyl laurate weight-hourly space velocity of 5.2 h⁻¹, the catalyst activity followed the order: Ni₂P > MoP > CoP-Co₂P > WP > Fe₂P-FeP; Ni ≈ Ni₂P > Ni₁₂P₅ > Ni₃P. The high activity is ascribed to the increases in surface metal site density, the electron density of metal site and Brønsted acidity. In contrast to metallic Ni, the nickel phosphides had much lower activities for methanation and cracking reaction due to the electronic and geometrical effects of P. The main products on the metallic Ni and the Ni, Co and Fe phosphides were C11 hydrocarbons formed via decarbonylation pathway, whereas the predominating products on MoP and WP were C12 hydrocarbons produced via hydrodeoxygenation pathway. The higher the electron density of metal site is, the more predominant the decarbonylation pathway. The increase in the interaction between metal site and oxygen promoted the hydrodeoxygenation pathway. Compared to metallic Ni and the Ni and Co phosphides that primarily gave n-alkanes, Fe, Mo and W phosphides additionally yielded alkenes and iso-hydrocarbons, which is attributed to their lower hydrogenation ability and higher Brønsted acidity. In all, we propose that the deoxygenation mechanism is mainly determined by the electron property of metal site and Brønsted acidity. Also, there might be a synergism between the metal and Brønsted acid site for the deoxygenation of methyl laurate.

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1. Introduction

Nowadays, fossil resources are rapidly being consumed, which simultaneously leads to serious environmental problem. Recently, triglyceride-based biomass is attracting great attention because it can be converted into renewable clean liquid fuels (sulfur-, nitrogen-free) [1]. This is very favorable to alleviate environmental problem. Through the catalytic transesterification, triglyceride-based biomass has commercially been used to produce biodiesel (mainly fatty acid methyl esters). Even though biodiesel is suitable for blending with petroleum-derived diesel fuels, it suffers from some problems in comparison with the petroleum-based diesel fuel, such as higher viscosity, higher cloud point temperature, poor thermal and chemical stability, and lower energy density [2]. Alternatively, the catalytic hydroprocessing of triglyceride-based feedstock yields deoxygenated and saturated diesel-like hydrocarbons (also namely green or renewable diesel in the literatures),

whose composition is similar to that of the petroleum-based diesel fuel. Thus, in contrast to biodiesel, green diesel has higher oxidation stability, lower specific gravity and higher cetane number. Also, the advantage of the hydroprocessing over the transesterification involves lower processing cost (50% that of transesterification), compatibility with current infrastructure, engine compatibility, and feedstock flexibility [3].

During the hydroprocessing, the deoxygenation of the triglyceride or carboxylic ester can be reached via hydrodeoxygenation (HDO) and decarbonylation/decarboxylation pathways. The HDO pathway consists of several consecutive reactions, during which oxygen is eliminated as H₂O and the generating hydrocarbon has the same number of carbon atoms to the corresponding fatty acid. The decarbonylation/decarboxylation pathway refers to a process where oxygen is removed as CO/CO₂ and the resulting hydrocarbon has one carbon atom less than the corresponding fatty acid.

The deoxygenation catalysts mainly include conventional metal sulfides (e.g., sulfided CoMo/Al₂O₃ and NiMo/Al₂O₃) and noble metals [4,5]. The monometallic Ni and Co sulfides give almost complete decarbonylation/decarboxylation hydrocarbons, while monometallic Mo sulfide yields almost exclusively HDO

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Table 1Surface areas, CO or H₂ uptakes, crystallite sizes and TOFs.

Catalyst	Ni/P ratio in precursor	BET surface area (m ² /g)	CO or H ₂ uptake ^a (μmol/g _{cat})	Crystallite size (nm)	Acid amount ^b (μmol/g)	B/L ^c
Ni/SiO ₂	–	–	29	10	105	–
Ni ₃ P-Ni/SiO ₂	3/1	420	83	12	114	–
Ni ₃ P-Ni ₁₂ P ₅ /SiO ₂	2.5/1	406	55	–	187	–
Ni ₁₂ P ₅ /SiO ₂	2/1	392	52	10	183	–
Ni ₂ P/SiO ₂	1/1	356	72	12	432	0.042
Ni ₂ P(1:2)/SiO ₂	1/2	252	67	10	396	–
CoP-Co ₂ P/SiO ₂	1/1	346	31	12	167	0.035
Fe ₂ P-FeP/SiO ₂	1/1	154	21	15	101	0.085
MoP/SiO ₂	1/1	214	99	–	447	0.98
WP/SiO ₂	1/1	359	21	–	396	0.73

^a H₂ uptake only for Ni/SiO₂.^b Obtained from NH₃-TPD.^c Obtained from DRIFTS of pyridine adsorption.

hydrocarbons [6–8]. It is proposed that the electronic property of the individual metal sulfides affects the adsorption of reactants and consequently the deoxygenation pathway [6,8,9]. In addition, it was found that SH[–] groups (Brønsted acid sites) on the sulfide catalysts primarily promote the decarboxylation/decarbonylation pathway and slightly influence the HDO pathway [10,11]. The noble catalysts give mostly hydrocarbons via the decarbonylation/decarboxylation pathway [12–14]. In addition, the Pd dispersion affected only the deoxygenation rate, but not the product distribution [15]. Apart from the deoxygenation reactions, the isomerization also occurs on the zeolite-supported catalysts [13].

Although the sulfide and noble metal catalysts have widely been investigated and the sulfide catalysts have been industrialized, they have some disadvantages in practice. For the sulfide catalysts, sulphiding agent (e.g. H₂S or CS₂) is indispensably added to the feedstock to avoid the catalyst deactivation. This leads to forming undesirable S-containing products and increasing investment [16]. The scant and expensive noble metals have a limit in the practical application. Similar to the noble metal catalysts, metallic Ni catalysts give the predominating decarbonylation/decarboxylation products. However, they also yield cracked products [14]. This not only reduces the hydrocarbon yield but also increases the H₂ consumption. Therefore, to develop new kinds of catalysts for the deoxygenation is very significant. For this reason, nitride [17], carbide [18] and Ni₂P [19,20] catalysts have recently been reported.

In near decades, transition metal phosphides have attracted great attention for hydrodenitrogenation/hydrodesulfurization [21–23] and hydrodechlorination [24]. Also, several researchers [19,25–29] have applied them for the deoxygenations of some bio-fuel model compounds (for example, 4-methylphenol, guaiacol, anisole and dibenzofuran). Yang et al. [19] reported that Ni₂P/SBA-15 gave much higher n-C₁₈/n-C₁₇ ratio than Ni/SBA-15 in the deoxygenation of methyl oleate although it had slightly lower activity. However, the performances of other metal phosphides for the deoxygenations of carboxylic esters are not clear. It is known that P sites in the phosphides have “ligand” (or electronic) and “ensemble” (or geometrical) effects on metal sites [30], and the metal phosphides have both metallic and acidic properties [27,31]. The effects of P and bifunctional property on the deoxygenation activity and mechanism on the metal phosphide catalysts are also not clear. To obtain the insight into the optimal catalyst for the deoxygenation of triglyceride-based biomass, this issue is very worth investigating.

In the present work, our aim is to investigate the relationship between the structure and performance of the metal phosphide catalysts and to give insight into the deoxygenation mechanism of methyl laurate as a model reactant. To lessen the support effect, silica was used as support. The different metal (Ni, Co, Fe, Mo and W) phosphides and the different nickel phosphides were prepared by the temperature-programmed reduction (TPR) methods. Their

properties were characterized by N₂ sorption, XRD, XPS, DRIFTS of adsorbed pyridine, NH₃-TPD, H₂-TPD, CO and H₂ chemisorption. Their performances were evaluated for the deoxygenations of methyl laurate as well as its intermediates (lauric acid, dodecanal and dodecanol). To better understand the role of P in the phosphides, Ni/SiO₂, MoO₂/SiO₂ and PO_x/SiO₂ were also prepared and investigated. We propose the factors affecting the catalyst activity, the origin of the HDO and decarbonylation pathways as well as the reaction mechanism.

2. Experimental

2.1. Catalyst preparation

A commercial silica (Qingdao Haiyang Chemicals Co. Ltd., Qingdao, China; BET surface area 548 m²/g) was used. The supported phosphide catalysts were prepared by the TPR method. Firstly, the catalyst precursors (i.e. supported metal phosphates) were prepared by the impregnation method. Silica was incipiently impregnated with a mixture aqueous solution of NH₄H₂PO₄ and a metal salt Ni(NO₃)₂·6H₂O, Co(NO₃)₂·6H₂O, Fe(NO₃)₃·9H₂O, (NH₄)₆Mo₇O₂₄·4H₂O or (NH₄)₆W₇O₂₄·6H₂O, followed by drying at 393 K for 12 h and calcination at 823 K for 4 h. To prepare different nickel phosphides, the precursors with the Ni/P ratios of 3/1, 2.5/1, 2/1, 1/1 and 1/2 were prepared, respectively. In the precursors of Mo, W, Fe and Co phosphide catalysts, the M/P (M=Mo, W, Fe and Co) ratios were designated as 1/1. Secondly, the phosphide catalysts were prepared from the precursors by the TPR process as the following program: heating from 293 to 523 K at 10 K/min and from 523 to 923 K at 1 K/min, maintaining at 923 K for 3 h and then cooling to room temperature. The H₂ (>99.9%) flow was set as 320 ml/min per gram of precursor. To avoid the drastic oxidation, the prepared catalysts were passivated before exposure to air. The denotation of catalysts is based on the phase compositions detected by the XRD method (see Table 1).

For comparison, Ni/SiO₂ and MoO₂/SiO₂ were prepared according to the following procedure: silica was incipiently impregnated with an aqueous solution of Ni(NO₃)₂ or (NH₄)₆Mo₇O₂₄, followed by drying at 393 K for 12 h, calcination at 823 K for 4 h and reduction with H₂ at 723 K for 60 min. In addition, a PO_x/SiO₂ sample with the P content of 6.9 wt.% was prepared by impregnating silica with an aqueous solution of NH₄H₂PO₄, followed by drying at 393 K for 12 h and calcination at 773 K for 4 h.

In all catalysts, the nominal metal mass contents were 15%.

2.2. Catalyst characterization

The reducibility of precursors and the acidity of catalysts were characterized by H₂-TPR and NH₃ temperature-programmed

desorption (NH₃-TPD), respectively. The surface metal density was measured by CO or H₂ chemisorption method. H₂-TPD was used to characterize the H₂ adsorption states on catalysts. Details of H₂-TPR, NH₃-TPD, H₂-TPD and CO or H₂ chemisorption are given in Supplementary material.

N₂ adsorption–desorption isotherm was measured on a Quantachrome QuadraSorb SI apparatus at 77 K. The BET equation was used to calculate the BET surface area. XRD patterns were obtained on a D8 Focus powder diffractometer using Cu-K α radiation ($\lambda = 0.15406$ nm). Crystallite size was calculated using the Scherrer equation. X-ray photoelectron spectroscopy (XPS) was performed using a PHI-1600 ESCA instrument with Mg K α radiation (1253.6 eV). Binding energies were determined with adventitious carbon (C1s at 284.6 eV) as the reference. Since the passivation can mask the nature electron states of the fresh catalysts, the passivated catalysts were sputter-cleaned with an Ar⁺ ion beam (4 kV, 25 mA) for 1 min.

Diffuse reflection Fourier-transform spectroscopy (DRIFTS) with a pyridine probe molecule was measured on a Thermo Nicolet 6700 spectrophotometer equipped with a Thermo Spectra-Tech P/N0030-102 chamber. The finely powdered passivated catalyst was pressed flat in the sample holder and reduced in a H₂ flow (120 ml/min) at 723 K for 60 min. The catalyst was then cooled to 373 K and flushed by a N₂ flow for 30 min, and a background spectrum was recorded. For pyridine adsorption, the catalyst was dosed at 373 K with a partial pressure of pyridine of 2.2% in a N₂ flow for 60 min. The catalyst was then purged in a N₂ flow for 30 min at 373 K to remove the gaseous and weakly adsorbed pyridine. The spectrum was recorded via subtracting the background one. The concentration ratio between Brønsted and Lewis acid sites (B/L) was determined by the method provided in references [32,33]. The procedure is given in Supplementary material.

2.3. Activity test

The deoxygenation of methyl laurate, lauric acid, dodecanal and dodecanol were tested on a continuous flow stainless-steel fixed-bed reactor (12 mm in diameter). In the blank reactor, there were very low conversion of the reactants and hydrocarbon yields (Table 1S in Supplementary material). The catalyst (0.15~0.30 mm in diameter) was diluted with quartz sand of the same diameter and supported on quartz cotton. A layer of quartz sand was placed on the catalyst bed to preheat the reactants. The passivated phosphide catalyst was re-reduced at 723 K for 60 min in a H₂ flow (>99.9%). Ni/SiO₂ and MoO₂/SiO₂ were in situ prepared from the corresponding precursors. After the reduction, the temperature and H₂ pressure were adjusted to the desired values. The reactant was continuously fed to the reactor using a pump. The reactor effluent was cooled to room temperature and the condensed liquid was collected in a liquid/gas separator. The liquid products were identified using gas chromatograph (GC) standards and an Agilent GC6890-MS5973N. The liquid products were quantitatively analyzed on a SP-3420 GC equipped with a FID and a HP-5 capillary column (30 m × 0.33 mm × 0.5 μ m). Tetrahydronaphthalene was used as internal standard for quantitative analysis. The gaseous effluent was analyzed on an on-line 102 GC equipped with a TCD and a TDX-101 packed column, and N₂ was used as internal standard for quantitative analysis.

The conversion of reactant (X) and the selectivity to product *i* (*S_i*) were defined as follows:

$$X = \frac{n_0 - n}{n_0} \times 100\%; S_i = \frac{n_i}{n_0 - n} \times 100\%$$

Where *n₀* and *n* denote the moles of reactant in the feed and the product, respectively; *n_i* denotes the mole of reactant

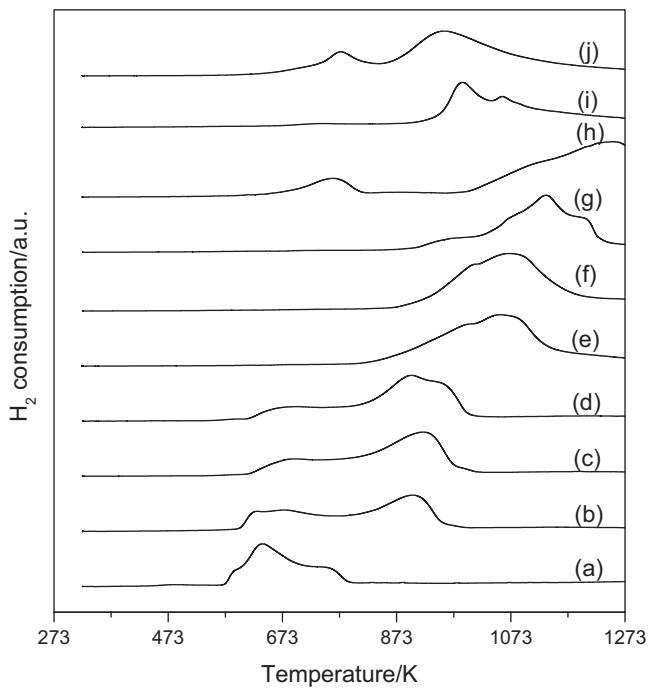


Fig. 1. H₂-TPR profiles of catalyst precursors (a) Ni/SiO₂; (b) Ni₃P–Ni/SiO₂; (c) Ni₃P–Ni₁₂P₅/SiO₂; (d) Ni₁₂P₅/SiO₂; (e) Ni₂P/SiO₂; (f) Ni₂P(1/2)/SiO₂; (g) CoP–Co₂P/SiO₂; (h) Fe₂P–FeP/SiO₂; (i) WP/SiO₂; (j) MoP/SiO₂.

converted to product *i* (for example, *n*-undecane, *n*-undecane and the oxygenated intermediates).

Hydrocarbon yield (*Y*) was used to identify the deoxygenation ability.

$$Y = \frac{\sum n_j}{n_0} \times 100\%$$

Where *n₀* and *n_j* denote the moles of reactant in the feed and hydrocarbon (C6–C12) in the product, respectively.

3. Results

3.1. Characterization of catalysts

3.1.1. H₂-TPR

Fig. 1 shows the H₂-TPR profiles of catalyst precursors. The Ni/SiO₂ precursor gave a main peak at about 640 K and a shoulder at higher temperature, which are ascribed to the reductions of bulk NiO and nickel silicate [27], respectively. For the nickel phosphide precursors, as the Ni/P ratio decreased, the initial and final reduction temperatures shifted to higher ones. This means that the existence of phosphate retarded the reduction of nickel species. For the precursors with the Ni/P ratios of 3/1, 2.5/1 and 2/1, there were two main peaks at about 671 and 920 K, which are probably attributed to NiO and nickel oxy-phosphates [34], respectively. The precursors with Ni/P ratios of 1/1 and 1/2 gave the main peaks at about 1060 and 1075 K, respectively. Such high temperature is ascribed to the formation of nickel phosphate [34]. The Co phosphide catalyst precursor gave several peaks between 880 and 1273 K that are ascribed to the reduction of Co phosphate [28,35]. In the profile of Fe phosphide precursor, the peak at about 760 K may be related to the reduction of Fe oxide, while the main peak at about 1250 K is ascribed to the reduction of Fe phosphate [35]. In the profile of the WP/SiO₂ precursor, a small peak at 745 K may be due to the reduction of W⁶⁺ species, while two peaks at about 988 and 1058 K are ascribed to the reduction of W phosphate. Two peaks at around 777 and 957 K are visible for the MoP/SiO₂

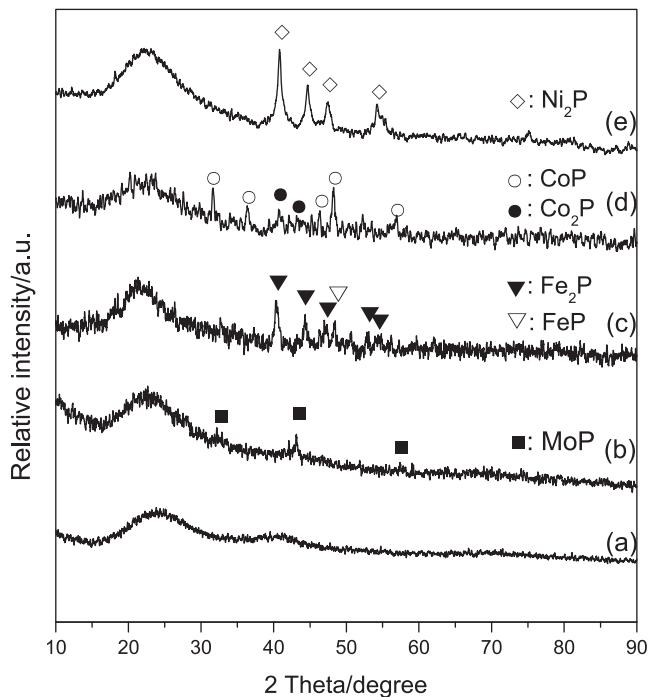


Fig. 2. XRD patterns of (a) WP/SiO₂; (b) MoP/SiO₂; (c) Fe₂P-FeP/SiO₂; (d) CoP-Co₂P/SiO₂; (e) Ni₂P/SiO₂.

precursor, which are ascribed to the reduction of Mo⁶⁺ to Mo⁴⁺ and the co-reduction of Mo⁴⁺ and phosphate [27,28], respectively. In all, for the iron group metal phosphates, the reducibility became difficult in the order of Ni, Co and Fe. The reduction of W phosphate was slightly more difficult than that of Mo phosphate. This tendency is consistent with that reported by Bui et al. [28].

3.1.2. XRD, N₂ sorption and CO uptake

Fig. 2 shows the XRD patterns of different metal phosphide catalysts prepared from the corresponding precursors with metal/P ratios of 1.0. In each pattern, the broad peak at about $2\theta = 22^\circ$ is ascribed to the amorphous silica. The peaks ($2\theta = 40.7^\circ, 44.5^\circ, 47.3^\circ$ and 54.1° , PDF 03-0953) due to Ni₂P are visible for Ni₂P/SiO₂. Both CoP ($2\theta = 31.6^\circ, 36.3^\circ, 46.2^\circ, 48.1^\circ$ and 56.7° , PDF 65-2593) and Co₂P ($2\theta = 40.8^\circ, 43.3^\circ$, PDF 32-0306) phases were formed on CoP-Co₂P/SiO₂, which is consistent with the report from Burns et al. [36]. Apart from the major Fe₂P phase ($2\theta = 40.3^\circ, 44.2^\circ, 47.3^\circ, 52.9^\circ, 54.3^\circ$, PDF 27-1171), the FeP phase ($2\theta = 48.5^\circ$, PDF 65-2595) was also detected for Fe₂P-FeP/SiO₂. The weak peaks ($2\theta = 32.1^\circ, 43.1^\circ$ and 57.4° , PDF 24-0771) due to MoP are observed for MoP/SiO₂. No peaks due to WP were detected for WP/SiO₂. Although the metal mass contents were same for all catalysts, the W atomic content was lower because of the larger W atomic weight. This leads to the well dispersed WP crystallites that were not detectable.

Fig. 3 shows the XRD patterns of Ni/SiO₂ and the nickel phosphide catalysts prepared from the precursors with different Ni/P ratios. There is only metallic Ni in Ni/SiO₂. Apart from major Ni₃P phase ($2\theta = 41.7^\circ, 42.8^\circ, 43.7^\circ, 45.3^\circ$ and 46.5° , PDF 65-2778), metallic Ni ($2\theta = 44.5^\circ$) was detected for Ni₃P-Ni/SiO₂ that was prepared from the precursor with the Ni/P ratio of 3, while Ni₁₂P₅ phase was detected in Ni₃P-Ni₁₂P₅/SiO₂ that was prepared from the precursor with the Ni/P ratio of 2.5. Ni₁₂P₅ phase ($2\theta = 38.6^\circ, 41.8^\circ, 44.6^\circ, 47.0^\circ$ and 49.0° , PDF 65-1623) was detected in the Ni₁₂P₅/SiO₂ prepared from the precursor with the Ni/P ratio of 2. The peaks due to Ni₂P are visible in the patterns of Ni₂P/SiO₂ and Ni₂P(1/2)/SiO₂. Clearly, the Ni/P ratio in the precursor determined the nickel phosphide phase. During the TPR process of the

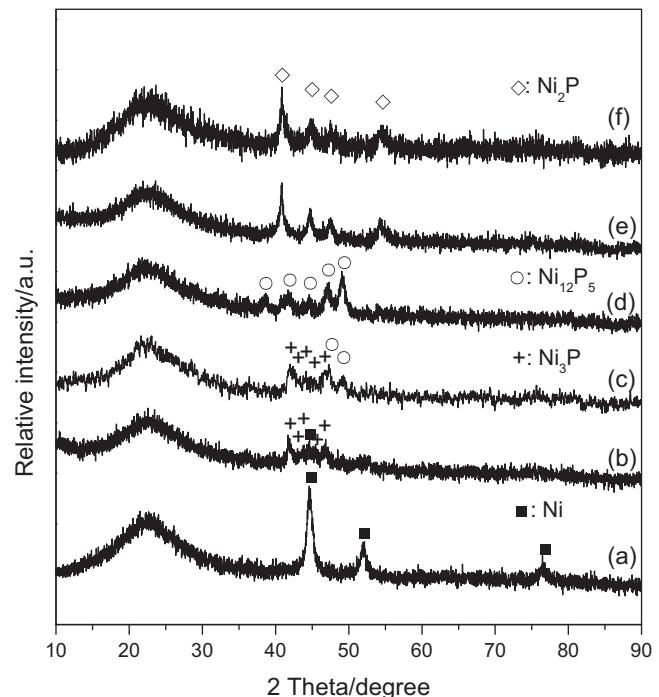


Fig. 3. XRD patterns of (a) Ni/SiO₂; (b) Ni₃P-Ni/SiO₂; (c) Ni₃P-Ni₁₂P₅/SiO₂; (d) Ni₁₂P₅/SiO₂; (e) Ni₂P/SiO₂; (f) Ni₂P(1/2)/SiO₂.

catalyst precursor, the phosphate was reduced to elemental P and P_xH_y (such as PH₃) that reacted with the reduced Ni atoms to form nickel phosphides. Meanwhile, some P_xH_y (such as PH₃) left the catalyst [34]. Due to the P loss, the Ni/P ratio in the precursor is needed to be lower than that in the objective nickel phosphide phase. This can account for the formation of Ni in Ni₃P-Ni/SiO₂.

Table 1 shows BET surface areas, crystallite sizes and CO uptakes of the phosphide catalysts. The BET surface areas ranged from 154 to 420 m²/g. For the nickel phosphide catalysts, the surface area decreased as the Ni/P ratio decreased. This is ascribed to the partial blockage of the pores by the phosphide and excess phosphorus species. The CO uptakes were between 21 and 99 μmol/g for all catalysts.

3.1.3. XPS

Fig. 4 shows the XPS spectra of the P 2p, Ni 2p_{3/2}, Co 2p_{3/2}, Fe 2p_{3/2}, Mo 3d and W 4f regions for the phosphide catalysts prepared from the precursors with the Ni/P ratios of 1. In P 2p XPS spectra, two P 2p peaks are observed at 129.2~129.6 and 133.9~134.6 eV, respectively. They are ascribed to the reduced P and PO₄³⁻, respectively. The reduced P atom is bonded to the metal atom in the phosphide, while PO₄³⁻ species are derived from the passivation and/or un-reduced ones. The reduced P had smaller electron binding energy than the element P (130.2 eV), indicating that it possesses negative charge via electron transfer from the metal. In other word, the metal site in the phosphide has positive charge. In the order of Fe₂P-FeP/SiO₂, CoP-Co₂P/SiO₂ and Ni₂P/SiO₂, the increase of the reduced P binding energy may indicate the decrease of the amount of the electron transfer from the metal to P [37].

For Ni₂P/SiO₂, two peaks are visible in the Ni 2p_{3/2} region at 853.4 and 856.9 eV, which are assigned to the Ni^{δ+} species in Ni₂P and Ni²⁺ [38], respectively. For CoP-Co₂P/SiO₂, the peaks at 778.3 and 781.5 eV in the Co 2p_{3/2} region are attributed to the Co^{δ+} species in Co phosphides and Co²⁺ [36], respectively. The peak at about 783 eV is assigned to the satellite one of Co^{δ+} derived from the bulk plasmon loss [39], while the peak at 786 eV is ascribed to the shake-up satellite one of Co²⁺. For Fe₂P-FeP/SiO₂, the peaks at 706.6 and

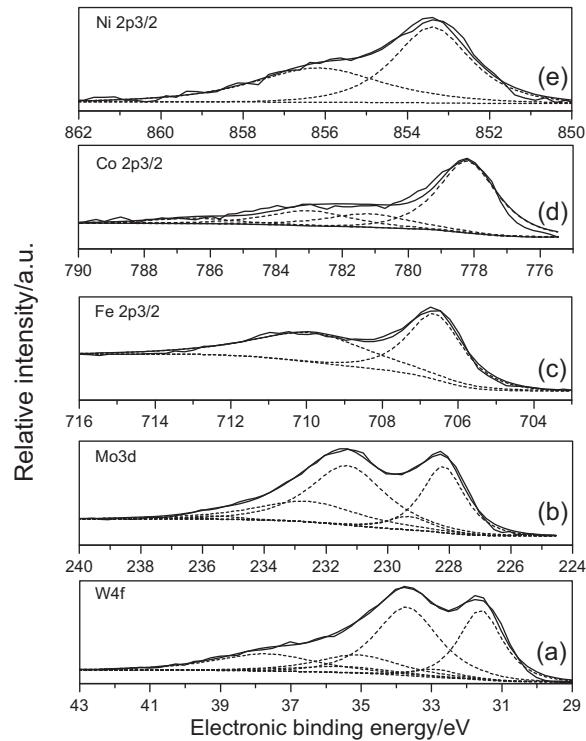
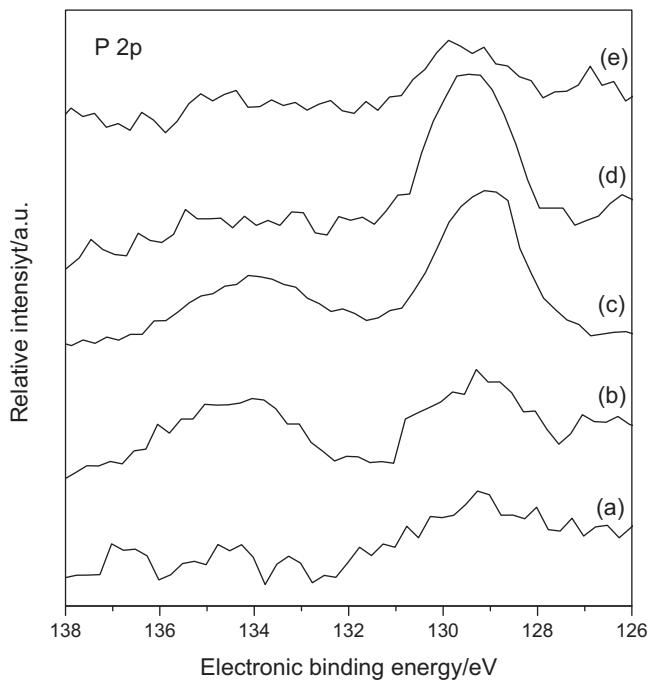


Fig. 4. XPS spectra of P 2p, W 4f, Mo 3d, Fe 2p_{3/2}, Co 2p_{3/2} and Ni 2p_{3/2} (a) WP/SiO₂; (b) MoP/SiO₂; (c) Fe₂P-FeP/SiO₂; (d) CoP-Co₂P/SiO₂; (e) Ni₂P/SiO₂.

710.5 eV in the Fe 2p_{3/2} region are attributed to the Fe^{δ+} species in Fe phosphides and Fe²⁺ [40], respectively. For MoP/SiO₂, the Mo 3d_{5/2} peaks at 228.3, 229.3 and 232.6 eV are attributed to the Mo^{δ+} species in MoP, Mo⁴⁺ and Mo⁶⁺ [41,42], respectively. The Mo 3d_{5/2} peak at 228.3 eV had a higher binding energy than that of metallic Mo (Mo⁰, 227.4–227.8 eV) [41], indicating that the reduced Mo has larger positive charge than Mo⁰. For WP/SiO₂, the W 4f_{7/2} peak at 31.6 eV and the W 4f_{5/2} peak at 33.7 eV are observed. They are attributed to the W^{δ+} in WP, which were higher than those (31.2 and 33.4 eV) of metallic W⁰ [43]. The W 4f_{7/2} peak at 32.9 eV and

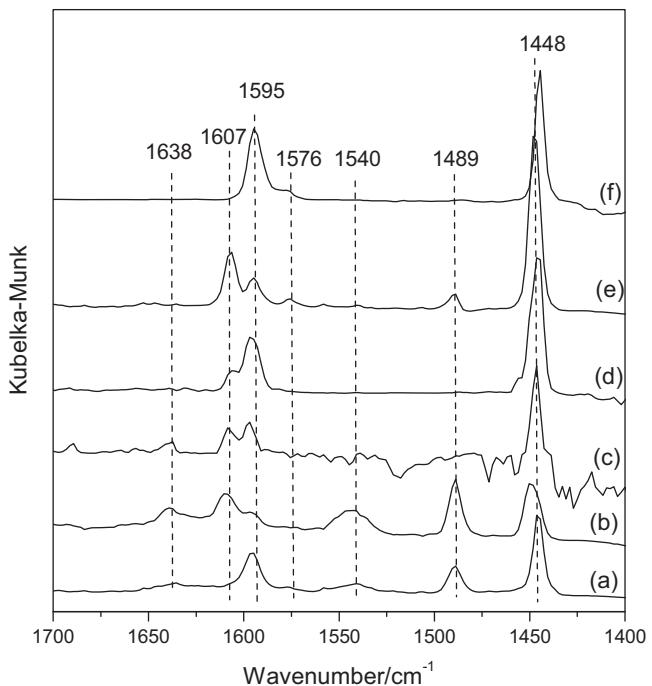


Fig. 5. In situ DRIFTS spectra of adsorbed pyridine on (a) WP/SiO₂; (b) MoP/SiO₂; (c) Fe₂P-FeP/SiO₂; (d) CoP-Co₂P/SiO₂; (e) Ni₂P/SiO₂.

the W 4f_{5/2} peak at 35.1 eV are ascribed to W⁴⁺ [43], and the W 4f_{7/2} peak at 35.5 eV and the W 4f_{5/2} peak at 37.7 eV are ascribed to W⁶⁺ [43,44].

3.1.4. DRIFTS of adsorbed pyridine

The surface acidity of the different phosphide catalysts was determined by DRIFTS of pyridine adsorption. Before the adsorption of pyridine, the passivated catalysts were re-reduced at 723 K for 1.0 h. In the DRIFTS spectra of the re-reduced phosphide catalysts, the adsorption band at 3665 cm⁻¹ is ascribed to the stretching mode of P-OH group (see Fig 1S in Supplementary material). This means that the P-OH group was produced on the re-reduced phosphide catalysts.

The DRIFTS spectra of pyridine adsorption in the region 1700–1400 cm⁻¹ are shown in Fig. 5. The bands at 1638, 1607, 1595, 1576, 1540, 1489 and 1448 cm⁻¹ are visible. According to the literatures [31,45], the bands at about 1448, 1576 and 1607 cm⁻¹ correspond to the vibrations of pyridine adsorbed on Lewis acid sites, the bands at about 1540 and 1638 cm⁻¹ correspond to the vibrations of pyridine adsorbed on Brønsted acid sites, and the band at about 1489 cm⁻¹ is related to the vibrations of pyridine adsorbed on both Brønsted and Lewis acid sites. In addition, the band at 1595 cm⁻¹ is ascribed to the vibration of hydrogen-bonded pyridine [45]. In each spectrum, the band at 1448 cm⁻¹ was stronger than that at 1540 cm⁻¹, indicating that the Lewis acidity might be dominant over the Brønsted one. Relative to the band at 1448 cm⁻¹, the bands at 1540 and 1638 cm⁻¹ were more obvious for MoP/SiO₂, WP/SiO₂ and Fe₂P-FeP/SiO₂ than for Ni₂P/SiO₂ and CoP-Co₂P/SiO₂. This means that MoP/SiO₂, WP/SiO₂ and Fe₂P-FeP/SiO₂ had more Brønsted acid sites (the B/L ratios shown in Table 1). For Ni/SiO₂, the adsorption of pyridine gave rise to the band at about 1448 cm⁻¹ and no band at 1540 cm⁻¹. This indicates that there was only Lewis acidity on Ni/SiO₂.

3.1.5. NH₃-TPD

Fig. 6 shows the NH₃-TPD profiles of the nickel phosphide catalysts, and the acid amounts of the catalysts are shown in Table 1.

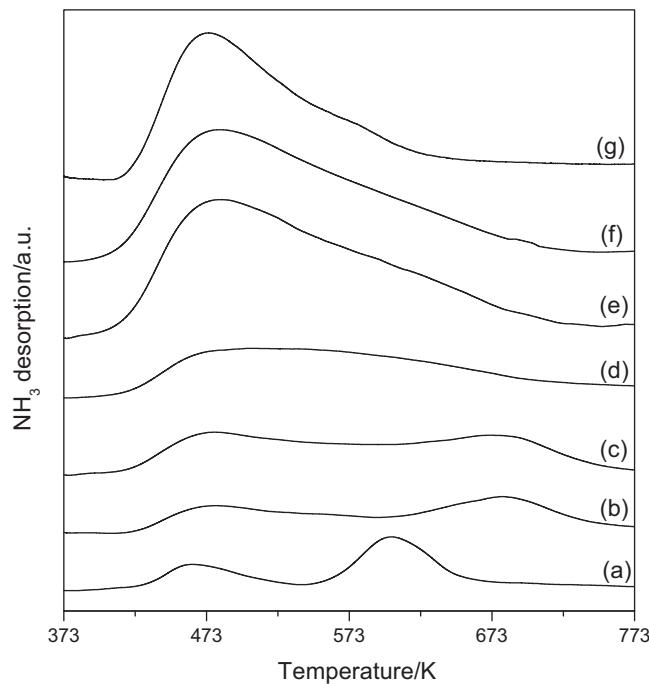


Fig. 6. NH₃-TPD profiles of (a) Ni/SiO₂; (b) Ni₃P-Ni/SiO₂; (c) Ni₃P-Ni₁₂P₅/SiO₂; (d) Ni₁₂P₅/SiO₂; (e) Ni₂P/SiO₂; (f) Ni₂P(1/2)/SiO₂; (g) PO_x/SiO₂.

For comparison, the NH₃-TPD profiles of Ni/SiO₂ and PO_x/SiO₂ are also presented. Ni/SiO₂ gave two peaks centered at about 463 and 603 K, which are probably related to acidities of SiO₂ and the un-reduced nickel silicate [46], respectively. In the trace of PO_x/SiO₂, the peak at about 473 K is mainly ascribed to the P-OH group [27]. In the traces of Ni₃P-Ni/SiO₂ and Ni₃P-Ni₁₂P₅/SiO₂, there were two peaks centered at about 478 and 678 K. For Ni₁₂P₅/SiO₂, there was a broad peak between 423~723 K, whereas no peak at 678 K was observed. Ni₂P/SiO₂ and Ni₂P(1/2)/SiO₂ gave a main peak centered at 483 K with a shoulder at higher temperature. As the Ni/P ratio increased, the acidity strength tended to decrease, whereas the acid amount first increased and then decreased. Among the nickel phosphide catalysts, the Ni₂P/SiO₂ had the most acid amount (Table 1). Fig. 7 shows the NH₃-TPD profiles of different metal phosphide catalysts. Each catalyst gave a main peak with a shoulder at higher temperature. The acid amount followed the order: MoP/SiO₂ > Ni₂P/SiO₂ > WP/SiO₂ > CoP-Co₂P/SiO₂ > Fe₂P-FeP/SiO₂ (Table 1).

3.1.6. H₂-TPD

Fig. 8 shows the H₂-TPD profiles of the nickel phosphide catalysts. For Ni/SiO₂, the H₂ desorption below 673 K is ascribed to the adsorbed H₂ on metal Ni sites, while the H₂ desorption above 673 K is usually ascribed to the spilt-over hydrogen [27]. In the range below 673 K, the nickel phosphide catalysts had higher H₂ desorption temperature in comparison with Ni/SiO₂. As the Ni/P ratio decreased, the desorption peak below 673 K shifted to lower temperature, and the H₂ desorption amount tended to increase. The similar tendency is for the H₂ desorption amount above 673 K. Ni₂P/SiO₂ had the most total H₂ desorption amount. In contrast to Ni/SiO₂, the nickel phosphide catalysts had more the spilt-over hydrogen. Fig. 9 shows the H₂-TPD profiles of different metal phosphide catalysts. The H₂ desorption amount below 673 K followed the sequence: MoP/SiO₂ > Ni₂P/SiO₂ > WP/SiO₂ ≈ CoP-Co₂P/SiO₂ > Fe₂P-FeP/SiO₂. The H₂ desorption amount above 673 K decreased in the order of WP/SiO₂ > CoP-Co₂P/SiO₂ > MoP/SiO₂ > Ni₂P/SiO₂ > Fe₂P-FeP/SiO₂.

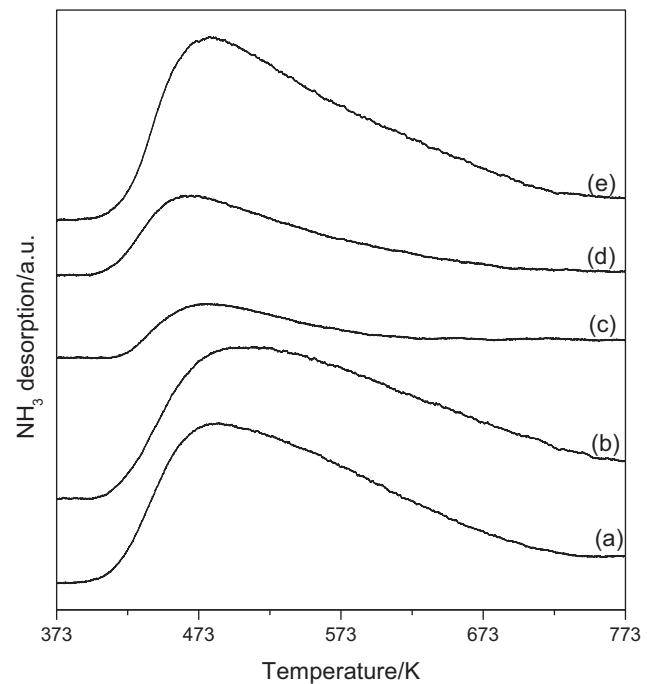


Fig. 7. NH₃-TPD profiles of (a) WP/SiO₂; (b) MoP/SiO₂; (c) Fe₂P-FeP/SiO₂; (d) CoP-Co₂P/SiO₂; (e) Ni₂P/SiO₂.

3.2. Catalytic reactivity

3.2.1. Reactivities of different metal phosphide catalysts in deoxygenation of methyl laurate

Table 2 shows the reactivities of different metal phosphide catalysts in the deoxygenation of methyl laurate. Under the condition of 573 K, 2.0 MPa, weight hourly space velocity (WHSV) of 5.2 h⁻¹ and H₂/methyl laurate ratio of 25, the conversion of methyl laurate followed the sequence: Ni₂P/SiO₂ > MoP/SiO₂ > CoP-Co₂P/SiO₂ > WP/SiO₂ > Fe₂P-FeP/SiO₂. The major hydrocarbon

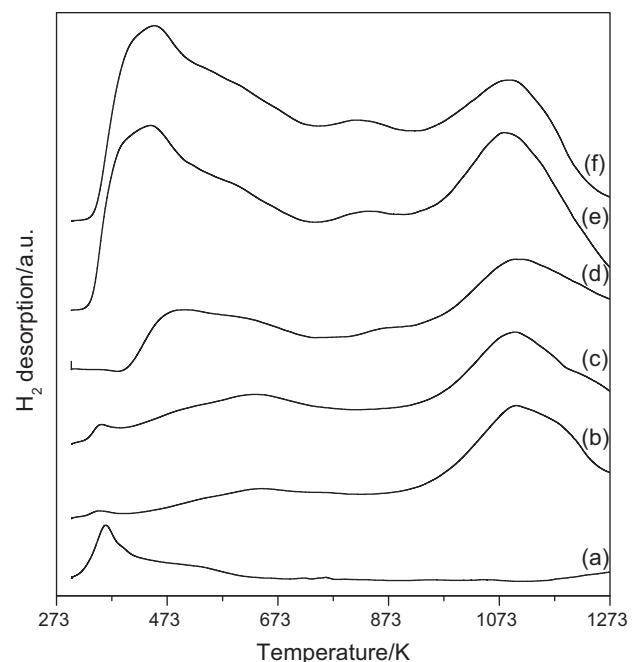


Fig. 8. H₂-TPD profiles of (a) Ni/SiO₂; (b) Ni₃P-Ni/SiO₂; (c) Ni₃P-Ni₁₂P₅/SiO₂; (d) Ni₁₂P₅/SiO₂; (e) Ni₂P/SiO₂; (f) Ni₂P(1/2)/SiO₂.

Table 2Deoxygenation of methyl laurate on different metal phosphide catalysts.^a

Catalyst	Conversion (%)	Y (%)	Selectivity (%)				C11/C12 (mol/mol)	CO/CH ₄ (mol/mol)	C11/CO (mol/mol)	
			C6–C10	C11 ^b	C12 ^c	Oxy. ^d				
Ni ₂ P/SiO ₂	95.9	95.4	0.3	82.9	16.3	0.6	99.2	5.1	3.6	1.0
CoP–Co ₂ P/SiO ₂	45.8	35.3	0.2	64.6	12.3	5.4	76.9	5.3	5.7	0.9
Fe ₂ P–FeP/SiO ₂	26.1	7.3	0.1	21.1 (1.5:1)	6.6 (1.6:1)	17.9	27.7	3.3	1.5	1.0
MoP/SiO ₂	62.8	46.5	0.3	2.7 (1.4:1)	71.1 (1.6:1)	13.0	73.8	0.04	0.3	1.1
WP/SiO ₂	39.9	22.5	0.4	2.1 (1.6:1)	53.9 (4.0:1)	16.5	56.1	0.04	0.1	1.1
PO _x /SiO ₂	29.9	1.3	0.4	2.9 (0.4:1)	1.0 (0.9:1)	11.3 (10.5 ^e)	3.9	2.8	–	–

^a Reaction conditions: 573 K, 2.0 MPa, H₂/methyl laurate = 25, WHSV = 5.2 h⁻¹.^b The data in parentheses indicate the ratio between undecene and *n*-undecane.^c The data in parentheses indicate the ratio between dodecene and *n*-dodecane.^d Oxygenated intermediates (including dodecanal, dodecanol, lauric acid and dodecyl laurate).^e Selectivity to lauric acid.

products on Ni₂P/SiO₂ and CoP–Co₂P/SiO₂ were *n*-C11 (*n*-undecane) and *n*-C12 (*n*-dodecane). Apart from *n*-C11 and *n*-C12, a great amount of alkenes (including undecene and dodecene) and few isoalkanes (including isoundecane and isododecane) were produced on Fe₂P–FeP/SiO₂, MoP/SiO₂ and WP/SiO₂. Ni₂P/SiO₂, CoP–Co₂P/SiO₂ and Fe₂P–FeP/SiO₂ gave the C11/C12 ratios higher than 1.0, whereas MoP/SiO₂ and WP/SiO₂ gave the C11/C12 ratios much lower than 1.0. The total selectivity to the C11 and C12 hydrocarbons (including alkanes, alkenes and isododecane) decreased in the order of Ni₂P/SiO₂ > CoP–Co₂P/SiO₂ > MoP/SiO₂ > WP/SiO₂ > Fe₂P–FeP/SiO₂, while the hydrocarbon yield followed the sequence: Ni₂P/SiO₂ > MoP/SiO₂ > CoP–Co₂P/SiO₂ > WP/SiO₂ > Fe₂P–FeP/SiO₂. In the liquid products, the oxygen-containing intermediates (including lauric acid, dodecanal, dodecanol and dodecyl laurate) and methanol were detected. The selectivity to the oxygen-containing intermediates followed the order of Ni₂P/SiO₂ < CoP–Co₂P/SiO₂ < MoP/SiO₂ < WP/SiO₂ < Fe₂P–FeP/SiO₂. As indicated in Table 2S in Supplementary material, lauric acid was the main intermediate, and there were more dodecyl laurate formed on Fe₂P–FeP/SiO₂, MoP/SiO₂ and WP/SiO₂. The detected gaseous products included CO and CH₄. The CO/CH₄ ratios on

Ni₂P/SiO₂, CoP/SiO₂ and FeP/SiO₂ exceeded 1.0, whereas those on WP/SiO₂ and MoP/SiO₂ were much lower than 1.0. In addition, the molar amount of CO was near to that of C11 hydrocarbons.

PO_x/SiO₂ was also found to catalyze the conversion of methyl laurate. It mainly catalyzed the decomposition of methyl laurate to lauric acid due to its Brønsted acidity. Both C11 and C12 hydrocarbons (including *n*-alkanes and alkenes) were formed on PO_x/SiO₂, and the C11/C12 ratio was larger than 1.0.

3.2.2. Reactivities of different nickel phosphide catalysts in deoxygenation of methyl laurate

As indicated above, Ni₂P/SiO₂ had the highest deoxygenation activity. Since there are different the nickel phosphide phases, the reactivities of different nickel phosphide catalysts were also tested (Table 3). For comparison, the reactivity of Ni/SiO₂ was also tested. On Ni/SiO₂ and nickel phosphide catalysts, the hydrocarbon products were *n*-C11 and *n*-C12. In the liquid products, the oxygen-containing intermediates (including dodecanal, dodecanol, lauric acid, dodecyl laurate) and methanol were detected, and the main intermediate was lauric acid (see Table 3S in Supplementary material). As the Ni/P ratio in the precursor decreased, the methyl laurate conversion and the total selectivity to *n*-C11 and *n*-C12 tended to increase. The Ni₂P catalysts gave the higher conversion and total selectivity to *n*-C11 and *n*-C12 than other nickel phosphide catalysts. Ni/SiO₂ gave the similar methyl laurate conversion to the Ni₂P catalysts, while it had lower total selectivity to *n*-C11 and *n*-C12 and higher selectivity to cracked products (including *n*-C6–*n*-C10). In addition, Ni/SiO₂ gave much higher *n*-C11/*n*-C12 ratio than the nickel phosphide catalysts. Thus, Ni/SiO₂ had higher activity for cracking and decarbonylation than the nickel phosphide catalysts. The *n*-C11/*n*-C12 ratio decreased in the sequence of Ni/SiO₂ < Ni₃P–Ni/SiO₂ < Ni₃P–Ni₁₂P₅/SiO₂ < Ni₁₂P₅/SiO₂ ≈ Ni₂P/SiO₂. This indicates that the decarbonylation pathway was inhibited due to P although it was always dominating over the HDO one on the nickel phosphide catalysts. In the gaseous effluent, CO and CH₄ were detected for the nickel phosphide catalysts, whereas nearly only CH₄ was detected on Ni/SiO₂. This indicates that CO was completely hydrogenated to CH₄ on Ni/SiO₂. The CO/CH₄ ratio on the nickel phosphide catalysts was larger than 1.0. In addition, the molar amount of CO was near to that of *n*-C11. On the metal phosphide catalysts, no CO₂ was detected and CO₂ was difficultly converted to CO or CH₄ (see Section 4.3.5), indicating that only decarbonylation took place.

3.2.3. Effects of temperature and space velocity on reactivities of Ni₂P/SiO₂ and MoP/SiO₂

As shown in Table 2, Ni₂P/SiO₂ and MoP/SiO₂ were more active than WP/SiO₂, CoP–Co₂P/SiO₂ and Fe₂P–FeP/SiO₂ in the deoxygenation of methyl laurate. Also, the C11/C12 ratios on Ni₂P/SiO₂ and MoP/SiO₂ were respectively 5.1 and 0.04, indicating that the

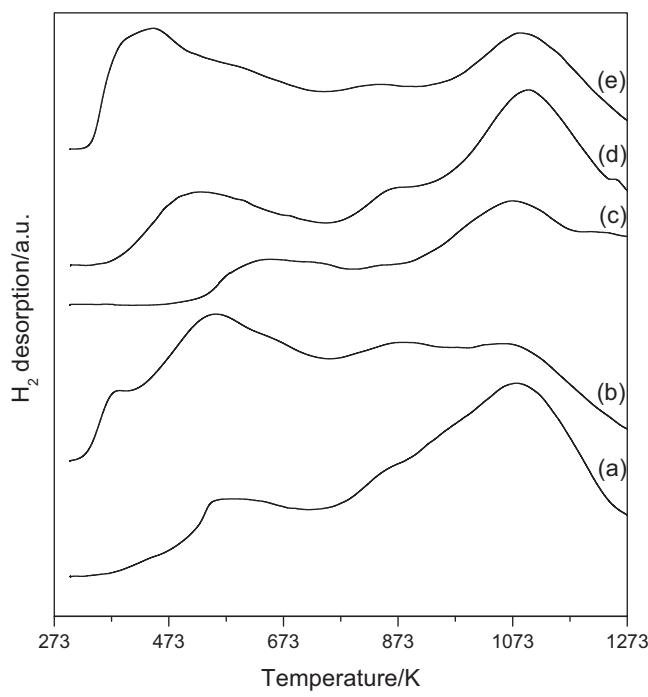
**Fig. 9.** H₂-TPD profiles of (a) WP/SiO₂; (b) MoP/SiO₂; (c) Fe₂P–FeP/SiO₂; (d) CoP–Co₂P/SiO₂; (e) Ni₂P/SiO₂.

Table 3Deoxygenation of methyl laurate on Ni/SiO₂ and nickel phosphide catalysts.^a

Catalyst	Conversion (%)	Y (%)	Selectivity (%)					<i>n</i> -C11/ <i>n</i> -C12 (mol/mol)	CO/CH ₄ (mol/mol)	<i>C</i> 11/ <i>C</i> 0 (mol/mol)
			C6–C10	<i>n</i> -C11	<i>n</i> -C12	Oxy. ^b	<i>n</i> -C11 + <i>n</i> -C12			
Ni/SiO ₂	95.1	94.7	4.1	93.0	2.5	0.5	95.5	37.8	– ^c	–
Ni ₃ P–Ni/SiO ₂	66.4	56.6	0.5	79.3	5.3	1.8	84.6	14.9	2.5	0.9
Ni ₃ P–Ni ₁₂ P ₅ /SiO ₂	53.6	41.9	0.2	70.2	7.9	4.6	78.1	8.9	2.6	0.9
Ni ₁₂ P ₅ /SiO ₂	70.6	67.7	0.4	81.1	14.5	2.5	95.6	5.6	3.4	1.0
Ni ₂ P/SiO ₂	95.9	95.4	0.3	82.9	16.3	0.6	99.2	5.1	3.6	1.0
Ni ₂ P(1:2)/SiO ₂	97.2	96.9	0.4	84.4	14.9	0.3	99.3	5.7	2.9	1.1

^a Reaction conditions: 573 K, 2.0 MPa, H₂/methyl laurate = 25, WHSV = 5.2 h^{–1}.^b oxygenated intermediates (including dodecanal, dodecanol, lauric acid and dodecyl laurate).^c Trace CO.

decarbonylation and HDO pathways were predominant on them, respectively. For insight into the reaction pathways, the reactivities of Ni₂P/SiO₂ and MoP/SiO₂ were evaluated under different temperatures and WHSVs.

Tables 4 and 5 show the reactivities of Ni₂P/SiO₂ and MoP/SiO₂ at different temperatures. As the temperature increased, the conversion, the selectivity to C11 and C12 and the hydrocarbon yield increased, while the selectivity to oxygenated intermediates decreased. Using Arrhenius equation, the apparent activation energies were calculated from the conversion rate (mol g_{cat}^{–1} s^{–1}) of methyl laurate, and they were 42.2 and 30.3 kJ/mol on Ni₂P/SiO₂ and MoP/SiO₂, respectively. The C11/C12 ratios on Ni₂P/SiO₂ and MoP/SiO₂ all increased with increasing temperature, indicating that the decarbonylation pathway was promoted. Even so, the HDO pathway was still predominant on MoP/SiO₂ because the C11/C12 ratio was much lower than 1.0. As the temperature increased, the selectivity to the cracked products increased on MoP/SiO₂, while it did not obviously changed on Ni₂P/SiO₂. For MoP/SiO₂, as the temperature increased, the isoalkanes/n-alkanes ratio increased, while the alkenes/n-alkanes ratio tended to decrease. The CO/CH₄ ratios on both Ni₂P/SiO₂ and MoP/SiO₂ decreased with increasing temperature.

Tables 4 and 5 also show the reactivities of Ni₂P/SiO₂ and MoP/SiO₂ at different WHSVs. As the WHSV decreased, the conversion, the total selectivity to C11 and C12, the hydrocarbon yield and the C11/C12 ratio increased, while the selectivity to the oxygenated intermediates decreased. For MoP/SiO₂, as the WHSV decreased, the isoalkanes/n-alkanes ratio increased, while the alkenes/n-alkanes ratio tended to decrease. The CO/CH₄ ratios decreased with decreasing WHSV.

3.2.4. Reactivities of Ni/SiO₂, Ni₂P/SiO₂, MoP/SiO₂ and PO_x/SiO₂ in deoxygenations of lauric acid, dodecanal and dodecanol

Lauric acid, dodecanal and dodecanol were detectable oxygenated intermediates during the conversion of methyl laurate. To explore the reaction mechanism, their conversions on Ni₂P/SiO₂ and MoP/SiO₂ was tested. To investigate the role of P-OH groups with Brønsted acidity, the reactivities of Ni/SiO₂ and PO_x/SiO₂ were also evaluated.

Table 6 shows that Ni/SiO₂ and Ni₂P/SiO₂ gave higher lauric acid conversions than MoP/SiO₂. PO_x/SiO₂ had the lowest conversion. On Ni/SiO₂, Ni₂P/SiO₂, MoP/SiO₂ and PO_x/SiO₂, the C11/C12 ratios and product distributions followed a similar trend to those in the deoxygenation of methyl laurate. In gaseous effluent, only CO was detected on Ni₂P/SiO₂, MoP/SiO₂ and PO_x/SiO₂, whereas only CH₄ was detected on Ni/SiO₂.

Tables 7 and 8 show the activities of the catalysts for the conversions of dodecanal and dodecanol. Dodecanal and dodecanol were nearly completely converted on Ni/SiO₂, MoP/SiO₂ and Ni₂P/SiO₂, indicating that they are very reactive. In the conversion of dodecanal on PO_x/SiO₂, a great deal of brown insoluble

substances was formed. This may be ascribed to the Brønsted sites that catalyzed the reactions (such as aldol condensation of aldehydes) to form heavy products [47]. On Ni/SiO₂, the product distribution and C11/C12 ratio in the deoxygenations of dodecanal and dodecanol had a similar trend to those in the deoxygenation of methyl laurate. In the deoxygenations of dodecanal and dodecanol, although the C11/C12 ratios on Ni₂P/SiO₂ were larger than 1.0, they were lower than those in the deoxygenations of lauric acid and methyl laurate. This means that, on Ni₂P/SiO₂, dodecanal and dodecanol are more prone to be deoxygenated via HDO pathway in comparison with lauric acid and methyl laurate. Apart from n-alkanes, alkenes and iso-alkanes were also formed on MoP/SiO₂ and PO_x/SiO₂ in the deoxygenations of dodecanal and dodecanol. The C11/C12 ratios on MoP/SiO₂ and PO_x/SiO₂ were between 0.02 and 0.14. Clearly, dodecanal and dodecanol were preferentially converted to C12 hydrocarbons on PO_x/SiO₂. This is very different from the case for methyl laurate and lauric acid.

The above results indicate that the deoxygenation pathway is affected by not only the catalyst property but also the kind of reactant.

4. Discussion

4.1. Property of metal phosphides

In this work, the prepared phosphides are metal-rich ones, in which the bonds between the metal and P atoms are covalent. In the metal phosphides, the P atoms possess ligand (or electronic) and ensemble (or geometrical) effects [30]. The ensemble effect influences the distance between the metal atoms [48], while the ligand effect induces a small charge transfer from metal to P [38]. The latter is clearly indicated by the XPS results (Fig. 4). However, the extent of the electron transfer very differs for the different metal phosphides. The positive charge (0~1) on the metal atom tends to decrease in the sequence of Fe, Co and Ni phosphides [37,39,49–51]. This is consistent with the electronegativity difference between the metal and the P atom, which follows the order: Fe < Co < Ni [51]. This is also reflected by the increase of binding energy of reduced P. In addition, as the Ni (or Co)/P ratio in the phosphides decreases, the positive charge of the metal site tends to increase [36,38]. Thus, it is reasonably speculated that the positive charge on Ni site follows the order: Ni < Ni₃P < Ni₁₂P₅ < Ni₂P. For MoP, the positive charge on Mo was estimated to be 0~4 [41,52]. The DFT calculation indicates that MoP has a less density of metal *d* states near the Fermi level than Ni₂P [50]. This indicates that the Mo site has larger positive charge than Fe, Co and Ni sites in the phosphides. Reasonably, the electronic property of W in WP is more similar to that of Mo in MoP rather than those of Ni, Co and Fe in the phosphides. Apart from the reduced Mo and W, there were also Moⁿ⁺ and Wⁿ⁺ (*n* = 4, 6) species on MoP/SiO₂ and WP/SiO₂ (Fig. 4), respectively. The Mo⁶⁺ and W⁶⁺ species might be formed during the catalyst passivation, and they

Table 4Deoxygenation of methyl laurate on $\text{Ni}_2\text{P}/\text{SiO}_2$ at different temperatures and WHSVs.^a

Temperature (K)	WHSV (h ⁻¹)	Conversion (%)	Y (%)	Selectivity (%)					$n\text{-C11}/n\text{-C12}$ (mol/mol)	CO/CH ₄ (mol/mol)
				C6~C10	$n\text{-C11}$	$n\text{-C12}$	Oxy. ^b	$n\text{-C11}+n\text{-C12}$		
533	5.2	49.4	20.2	0.3	30.2	10.7	6.5	40.9	2.8	2.8
553	5.2	72.5	60.6	0.2	66.3	17.1	2.5	83.3	3.9	3.7
573	5.2	95.9	95.4	0.3	82.9	16.3	0.6	99.2	5.1	3.6
593	5.2	98.8	98.4	0.3	88.8	10.5	0.5	99.3	8.4	2.3
613	5.2	99.5	99.0	0.4	90.2	8.9	0.5	99.1	10.2	1.6
573	4.0	97.6	97.3	0.3	83.2	16.3	0.3	99.5	5.1	3.2
573	7.4	89.7	88.9	0.3	82.4	16.5	0.8	98.9	5.0	3.9
573	10.4	72.6	63.2	0.4	72.1	14.9	1.7	87.0	4.8	4.2
573	17.3	56.4	47.6	0.4	69.0	15.4	1.9	84.4	4.6	4.2

^a Reaction conditions: 2.0 MPa, H₂/methyl laurate = 25.^b Oxygenated intermediates (including dodecanal, dodecanol, lauric acid and dodecyl laurate).**Table 5**Deoxygenation of methyl laurate on MoP/SiO_2 at different temperatures and WHSVs.^a

Temperature (K)	WHSV (h ⁻¹)	Conversion (%)	Y (%)	Selectivity (%)					$C11/C12$ (mol/mol)	CO/CH ₄ (mol/mol)
				C6~C10	$C11^b$	$C12^c$	Oxy. ^d	$C11+C12$		
573	5.2	62.8	46.5	0.3	2.7 (0.03:1.4:1)	71.0 (0.01:1.6:1)	13.0	73.8	0.04	0.27
593	5.2	79.4	72.9	0.4	3.6 (0.05:0.6:1)	87.8 (0.02:1.2:1)	4.4	91.4	0.04	0.24
613	5.2	95.1	87.0	0.6	4.2 (0.1:0.7:1)	86.8 (0.1:0.9:1)	0.5	90.9	0.05	0.15
633	5.2	98.1	89.7	1.7	6.2 (0.1:1.0:1)	83.6 (0.5:0.5:1)	0.2	89.7	0.07	0.14
573	2.6	84.3	69.3	0.8	6.0 (0.03:0.3:1)	75.3 (0.1:1.8:1)	4.2	81.4	0.08	0.11
573	1.5	91.6	82.7	0.7	8.3 (0.03:0.2:1)	81.3 (0.2:1.2:1)	3.4	89.6	0.1	0.07

^a Reaction conditions: 2.0 MPa, H₂/methyl laurate = 25.^b The data in parentheses indicate the ratio between iso-undecane, undecene and *n*-undecane.^c The data in parentheses indicate the ratio between iso-dodecane, dodecene and *n*-dodecane.^d Oxygenated intermediates (including dodecanal, dodecanol, lauric acid and dodecyl laurate).**Table 6**Deoxygenation of lauric acid on Ni/SiO_2 , $\text{Ni}_2\text{P}/\text{SiO}_2$, MoP/SiO_2 and PO_x/SiO_2 .^a

Catalyst product	Conversion (%)	Selectivity (%)					$C11/C12$ (mol/mol)	Gaseous
		C6~C10	$C11^b$	$C12^c$	Oxy. ^d	$C11+C12$		
Ni/SiO_2	95.6	7.1	79.6	2.5	2.6	82.1	32	CH ₄
$\text{Ni}_2\text{P}/\text{SiO}_2$	98.8	0.2	87.9	11.6	0.3	99.5	7.6	CO
MoP/SiO_2	73.1	0.1	4.0 (1.4:1)	23.3 (3.5:1)	20.6 (15.8 ^e)	27.3	0.2	CO
PO_x/SiO_2	42.4	–	4.8 (3.1:1)	1.3 (4.0:1)	1.3	6.1	3.8	CO

^a Reaction conditions: 573 K, 2 MPa, H₂/lauric acid = 25, WHSV = 6.0 h⁻¹, concentration of lauric acid in cyclohexane solution = 20 wt.%.^b The data in parentheses indicate the ratio between undecene and *n*-undecane.^c The data in parentheses indicate the ratio between dodecene and *n*-dodecane.^d Oxygenated intermediates (including dodecanal, dodecanol and dodecyl laurate).^e Dodecyl laurate.**Table 7**Deoxygenation of dodecanal on Ni/SiO_2 , $\text{Ni}_2\text{P}/\text{SiO}_2$, MoP/SiO_2 and PO_x/SiO_2 .^a

Catalyst	Conversion (%)	Selectivity (%)					$C11/C12$ (mol/mol)	Gaseous product
		C6~C10	$C11^b$	$C12^c$	C11+C12			
Ni/SiO_2	99.9	56.1	40.9	0.7	41.6	56.7	CH ₄	
$\text{Ni}_2\text{P}/\text{SiO}_2$	99.9	0.1	49.2	45.8	95.0	1.1	CO	
MoP/SiO_2	99.7	1.3	6.5 (0.1:0.2:1)	66.6 (0.5:0.6:1)	73.1	0.1	CO	
PO_x/SiO_2	75.2	0	1.4 (0.4:1.2:1)	9.7 (0.4:5.7:1)	11.1	0.1	–	

^a Reaction conditions: 573 K, 2 MPa, H₂/dodecanal = 25, WHSV = 6.0 h⁻¹.^b The data in parentheses indicate the ratio between iso-undecane, undecene and *n*-undecane.^c The data in parentheses indicate the ratio between iso-dodecane, dodecene and *n*-dodecane.**Table 8**Deoxygenation of dodecanol on Ni/SiO_2 , $\text{Ni}_2\text{P}/\text{SiO}_2$, MoP/SiO_2 and PO_x/SiO_2 .^a

Catalyst	Conversion (%)	Selectivity (%)					$C11/C12$ (mol/mol)	Gaseous product
		C6~C10	$C11^b$	$C12^c$	C11+C12			
Ni/SiO_2	99.9	34.7	63.2	2.0	65.2	31.9	CH ₄	
$\text{Ni}_2\text{P}/\text{SiO}_2$	99.8	0.8	52.1	40.8	92.9	1.3	CO	
MoP/SiO_2	99.8	1.3	4.1 (1.2:1.5:1)	69.0 (1.4:0.2:1)	73.1	0.06	CO	
PO_x/SiO_2	89.7	0.1	1.0 (0.04:0.2:1)	62.3 (0.2:13.9:1)	63.3	0.02	–	

^a Reaction conditions: 573 K, 2 MPa, H₂/dodecanol = 25, WHSV = 6.0 h⁻¹.^b The data in parentheses indicate the ratio between iso-undecane, undecene and *n*-undecane.^c The data in parentheses indicate the ratio between iso-dodecane, dodecene and *n*-dodecane.

were only reduced to Mo^{4+} and W^{4+} at 723 K [42,53], respectively. Indeed, $\text{MoO}_3/\text{SiO}_2$ was only reduced to $\text{MoO}_2/\text{SiO}_2$ at 723 K (see Fig. 2S in Supplementary material). Moreover, it was found that the Mo^{6+} species still existed when the passivated MoP/SiO_2 was re-reduced at 773 K [54].

The “ligand” and “ensemble” effects of P influence the interaction between CO or H_2 and metal sites in the phosphides [55,56]. Here, unlike Ni/SiO_2 with H_2 uptake of $29 \mu\text{mol/g}_{\text{cat}}$, the nickel phosphide catalysts had much lower H_2 uptakes ($<1.0 \mu\text{mol/g}_{\text{cat}}$). However, the H_2 -TPD profiles show that the nickel phosphide catalysts gave more desorbed H_2 than Ni/SiO_2 . This contradictory can be ascribed to the following reasons: (1) P may occupy nickel 3-fold hollow sites where favor the dissociative adsorption of H_2 [57]; (2) there is low interaction between H_2 and the Ni site on nickel phosphides [55,56]. These probably lead to a slow H_2 adsorption on the nickel phosphides. Unlike the H_2 uptake that was measured by the pulse technique, H_2 adsorption was held for 30 min before H_2 -TPD, which may be enough for complete H_2 adsorption. Since CO does not adsorb on nickel 3-fold hollow [57], the nickel phosphide catalysts gave larger CO uptakes than H_2 ones. In addition, as the Ni/P ratios decreased, the change tendency of CO uptakes was not completely consistent with that of the H_2 desorption amounts below 673 K (see Fig. 8 and Table 1). This indicates that there were different sites for H_2 and CO adsorptions. Apart from adsorption on Ni site, H_2 may also adsorb on Ni-P bridge site as well as P site [55,56]. Again, the P-OH groups on nickel phosphide crystallites probably contribute to the H_2 desorption. In addition, they also increase the amount of spilt-over hydrogen [24,58].

The metal phosphides have not only metallic property but also acidity. As shown in Fig. 5, the metal phosphide catalysts possessed both Brønsted and Lewis acidities, which are ascribed to the P-OH groups and the metal sites [31], respectively. Relative to the Lewis acid sites, there were obviously more Brønsted acid sites on MoP/SiO_2 , WP/SiO_2 and $\text{Fe}_2\text{P}-\text{FeP}/\text{SiO}_2$ than those on $\text{Ni}_2\text{P}/\text{SiO}_2$ and $\text{CoP}-\text{Co}_2\text{P}/\text{SiO}_2$. The more Brønsted acid sites on MoP/SiO_2 and WP/SiO_2 may be ascribed to Mo-OH and W-OH groups formed during the reduction process [42,47,53]. For the nickel phosphide catalysts, as the Ni/P ratio decreased, the acid amount first increased and then decreased. The former case is mainly ascribed to the increase of P content, while the latter may be attributed to the aggregation of P species as well as the decreased of the exposed of Ni sites. In addition, there was a similar change tendency for the H_2 and NH_3 desorption amounts. This may be ascribed to the two reasons: (1) metal site can adsorb not only NH_3 but also H_2 ; (2) the P-OH group can adsorb NH_3 and also favor the H storage and the formation of spilt-over hydrogen [58].

4.2. Catalytic activity for conversion of methyl laurate

As shown in Table 2, the methyl laurate conversion and the hydrocarbon yield decreased in the order of $\text{Ni}_2\text{P}/\text{SiO}_2 > \text{MoP}/\text{SiO}_2 > \text{CoP}-\text{Co}_2\text{P}/\text{SiO}_2 > \text{WP}/\text{SiO}_2 > \text{Fe}_2\text{P}-\text{FeP}/\text{SiO}_2$. The conversion of methyl laurate occurred not only on metal site but also on Brønsted acid site, especially the former. The catalyst having more surface metal sites should have higher activity. However, $\text{Ni}_2\text{P}/\text{SiO}_2$ gave higher activity than MoP/SiO_2 although it had less CO uptake. This may be ascribed to the higher electron density of Ni site in Ni_2P . On one hand, the high electron density of metal site favors the electron transfer from the metal site to the lowest unoccupied molecular orbital (LUMO) of C-O band [25], which facilitates the conversion via the dissociation of the C-O bond. On the other hand, the high electron density promoted the conversion via decarbonylation (see Section 4.3.1). Apart from the metal sites, the P-OH group (i.e., the Brønsted acid site) also catalyzed the conversion of methyl laurate. The P-OH group can

provide H^+ to catalyze the decarbonylation reaction [10,16] or to hydrogenate C=O group [59] as well as hydrolyze methyl laurate. WP/SiO_2 and $\text{Fe}_2\text{P}-\text{FeP}/\text{SiO}_2$ had similar CO uptakes, whereas WP/SiO_2 had higher activity than $\text{Fe}_2\text{P}-\text{FeP}/\text{SiO}_2$. This may be due to more Brønsted acid sites on WP/SiO_2 . We propose that there might also be a synergism between the metal site and the P-OH group. This can further be indicated by the activities of the nickel phosphide catalysts.

As the Ni/P ratio in the precursor decreased, the methyl laurate conversion and the hydrocarbon yield on the corresponding catalyst tended to increase. This tendency cannot be well explained by the electron density of Ni site since the electron density tends to decrease in the order of $\text{Ni}_3\text{P} < \text{Ni}_{12}\text{P}_5 < \text{Ni}_2\text{P}$. Also, this is not completely consistent with the CO uptake. Therefore, we speculate that the P-OH groups also influenced the activities of the nickel phosphide catalysts because their amount tended to increase as the Ni/P ratio decreased. As the Brønsted acid sites, the P-OH groups not only hydrolyzed methyl laurate but also assisted the conversion of methyl laurate adsorbed and activated on the Ni sites via hydrogenation or decarbonylation. The C11/C12 ratio indicates that the HDO pathway was promoted as the Ni/P ratio decreased. The C=O group activated on metal site might be hydrogenated by the hydrogen species from the adjacent P-OH groups. The synergism between the P-OH and Ni site was also found for the hydrodechlorination of chlorobenzene [60].

In short, increasing the amount of metal site, the electron density of metal site and the Brønsted acid site is favorable for enhancing the catalyst activity. Also, there might be a synergism between the metal and Brønsted acid site for the conversion of methyl laurate.

4.3. Deoxygenation mechanism

4.3.1. Deoxygenation of methyl laurate

In the deoxygenation of methyl laurate, C11 and C12 hydrocarbons were derived from the decarbonylation and HDO pathways, respectively. The C11/C12 ratio represents the selectivity between the decarbonylation and HDO pathways. As shown in Tables 2 and 3, the decarbonylation pathway mainly occurred on Ni/SiO_2 and Ni, Co and Fe phosphide catalysts, while the HDO one was dominating on WP/SiO_2 and MoP/SiO_2 .

PO_x/SiO_2 also gave C11 and C12 hydrocarbons, which should be ascribed to the role of the P-OH group (i.e., Brønsted acid site). The larger C11/C12 ratio than 1.0 indicates that the P-OH group alone more preferentially catalyzed the decarbonylation pathway than the HDO one. The role of the P-OH groups is similar to that of SH^- groups on the sulfide catalysts [10,11]. However, in contrast to the phosphide catalysts, PO_x/SiO_2 had much lower deoxygenation activity. Therefore, the primary active sites for the deoxygenation should be the metal ones, whose property determines the deoxygenation pathways.

Compared to Ni/SiO_2 , the nickel phosphide catalysts had much lower C11/C12 ratios (i.e., lower selectivity to the decarbonylation pathway). As the Ni/P ratio decreased, the C11/C12 ratio tended to decrease. Thus, the P site in nickel phosphides had an important influence on the deoxygenation pathways. This may be related to its ligand effect, leading to a small positive charge on Ni site in nickel phosphide. Associating with the positive charge on Ni site that follows the order of $\text{Ni} < \text{Ni}_3\text{P} < \text{Ni}_{12}\text{P}_5 < \text{Ni}_2\text{P}$, we found that the larger the positive charge of Ni site was, the lower C11/C12 ratio was. This tendency is also reflected from that on other phosphide catalysts.

Similar to the nickel phosphide catalysts, $\text{Fe}_2\text{P}-\text{FeP}/\text{SiO}_2$ and $\text{CoP}-\text{Co}_2\text{P}/\text{SiO}_2$ mainly gave the decarbonylation product (i.e., C11/C12 ratio > 1). However, MoP/SiO_2 and WP/SiO_2 dominantly gave the HDO product (i.e., C11/C12 ratio < 1). In the references,

it has been reported that the HDO pathway is dominating on the Mo-based catalysts (such as Mo_2S [6,8], Mo_2N [17], Mo_2C [18] and Mo [61]), while the decarbonylation/decarboxylation pathway is predominant on the sulfided Ni and Co catalysts [6–8]. Here, $\text{MoO}_2/\text{SiO}_2$ was also found to mainly yield the HDO hydrocarbons (Table 4S in Supplementary material). Clearly, the metal property is important for the deoxygenation pathway, perhaps affecting the interaction between the metal site and the oxygen in reactants. In the phosphides, the Mo and W sites had larger positive charges than Fe, Co and Ni sites. Also, there were Mo^{4+} and W^{4+} on MoP/SiO_2 and WP/SiO_2 , respectively. The positive charge determines the electrophilicity of metal site, while the electrophilicity affects the oxygen adsorption.

There have been many reports about the surface adsorptions and reactions of the oxygenated compounds on Ru [62], Pd [63–66], Ni [67–69], Fe [70–72] and Mo [61,73] surfaces. The surface oxygenated intermediates derived from alcohol, aldehyde, acid and ester include alkoxide, $\eta^1(\text{O})$ and $\eta^2(\text{C},\text{O})$ -aldehyde, carboxylate and $\eta^1(\text{C})$ -acyl (see Fig. 10) [63]. Among them, $\eta^1(\text{C})$ -acyl group is a common one adsorbed on metal site [62–73]. It is either hydrogenated to form alcohol via the activation of $\text{C}=\text{O}$ group or directly decarbonylates to CO and hydrocarbon. For the metal phosphides, the Mo and W sites have larger electrophilicity than the Fe, Co and Ni sites, and so they may preferentially adsorb the O atom of the $\text{C}=\text{O}$ group. As a result, the $\text{C}=\text{O}$ group was activated and hydrogenated to produce the HDO product. Additionally, the bond energy of carbonyl becomes less when the metal site is a better electron acceptor [69]. In comparison with that on the Fe phosphide, the higher C11/C12 ratios on the Ni and Co phosphides are also related to the smaller positive charges on Ni and Co sites. In the order of Ni, Ni_3P , Ni_{12}P and Ni_2P , the increased electrophilicity of Ni site leads to the decreased C11/C12 ratio. Clearly, enhancing the electrophilicity of metal site favorably activates the $\text{C}=\text{O}$ group via oxygen adsorption and subsequently promotes the HDO pathway. Similar opinion has also been suggested by other researchers [9,62,69,74]. In addition, the increase in metal–oxygen bond strength may also favor the activation of the C–O bond to give HDO products. DFT calculation [61] shows that, due to strong Mo–O bond, acetaldehyde decomposes via the C–O bond scissions rather than the C–C bond breaking on the clean Mo(110) surface. It has been reported that the metal–oxygen bond strength increases in order of Ni < Fe < W [75].

Apart from influencing the oxygen adsorption, the electronic property of metal site also affects the activation of β -C–H bond in $\eta^1(\text{C})$ -acyl or carboxylate intermediate, while the cleavage of β -C–H bond is the rate-determining step for the decarbonylation of $\eta^1(\text{C})$ -acyl or the decarboxylation of carboxylate [63,65,68,76]. The C–H bond activation is primarily guided by the electron-back donation to the anti-bonding σ_{CH^*} orbital [76,77], and so the C–H bond breaking is promoted by increasing the electron density of the metal site [66,72,73]. This is quite consistent with the present result. In the order of Ni, Ni_3P , Ni_{12}P and Ni_2P , the reduced electronic density of Ni site inhibited the decarbonylation, leading to the decrease of the C11/C12 ratio. The Mo and W sites had lower electron density than Ni, Co and Fe ones, and so they gave lower activity for the C–C bond cleavage. However, the low electron density favors the hydrogenation of acetyl [76]. This also gives rise to the dominating HDO pathway on MoP/SiO_2 and WP/SiO_2 .

The above discussion concerns the electronic property of metal site on the deoxygenation pathway. Usually, the electronic and geometrical effects occur simultaneously. In metal phosphides, the ensemble effect of P changes the distance between the metal atoms. This also influences the adsorption of the reactants. However, the electronic effect seems to be more predominant.

Apart from the catalyst property, the reaction condition also influenced the deoxygenation pathway. For $\text{Ni}_2\text{P}/\text{SiO}_2$ and

MoP/SiO_2 , the increase of the temperature favored the decarbonylation pathway (Tables 4 and 5). This is consistent with that the decarbonylation is endothermic and the hydrodeoxygenation is exothermic [1]. In addition, the decrease of WHSV also promoted the decarbonylation, where its influence was much lower than that of temperature.

4.3.2. Deoxygenation of lauric acid, dodecanal and dodecanol

As indicated in Section 3.2.4, the deoxygenation pathway is related to not only the catalyst property but also the kind of reactants.

Considering the C11/C12 ratios on Ni/SiO_2 , $\text{Ni}_2\text{P}/\text{SiO}_2$ and PO_x/SiO_2 , we suggest that the Ni site (especially with high electron density) preferentially catalyzed the decarbonylation reaction in the deoxygenations of methyl laurate and its intermediates. The P–OH group favorably catalyzed the decarbonylation reaction in the conversions of methyl laurate and lauric acid, whereas it preferentially catalyzed the HDO reaction in the conversions of dodecanal and dodecanol. When methyl laurate or lauric acid was the starting reactant, it could easily be converted to form adsorbed laurate on metal site [63]. Laurate was converted to either C11 hydrocarbon via decarbonylation or dodecanoyl via hydrogenolysis. However, there might be insufficient hydrogen required for the dodecanoyl hydrogenation due to the adsorption of methyl laurate or lauric acid on metal site [8]. This not only inhibited the hydrogen adsorption but also consumed hydrogen due to the hydrogenolysis. Because of no enough H_2 for hydrogenation, the decarbonylation was preferred. When dodecanal was the starting reactant, there were more available hydrogen species for its hydrogenation; moreover, the hydrogenation of dodecanal could also be catalyzed by the Brønsted acid sites (i.e., P–OH groups) on the catalysts. Compared to that of $\text{Ni}_2\text{P}/\text{SiO}_2$, the higher decarbonylation activity of Ni/SiO_2 in the deoxygenation of dodecanal can be ascribed to its higher metallic property (i.e., high electron density) and less Brønsted acidity. The Brønsted acidity of $\text{Ni}_2\text{P}/\text{SiO}_2$ led to its lower C11/C12 ratios in the deoxygenations of dodecanal and dodecanol than those in the deoxygenations of methyl laurate and lauric acid. Because MoP/SiO_2 had high electrophilicity of Mo site and Brønsted acidity, it catalyzed the deoxygenations of methyl laurate and its intermediates mainly via the HDO pathway.

In the conversion of dodecanol, the C11/C12 ratio followed similar trend in the conversion of dodecanal rather than those of methyl laurate and lauric acid. On one hand, dodecanol could be dehydrogenated to produce dodecanal on metal site followed by the decarbonylation. This can be supported by that Ni [63] and $\text{Ni}_2\text{P}/\text{SiO}_2$ [33] can dehydrogenate ethanol to acetaldehyde. For $\text{Ni}_2\text{P}/\text{SiO}_2$, the formation of CO in the conversion of dodecanol further confirms the dehydrogenation/decarbonylation mechanism. Ni/SiO_2 could also catalyze the hydrogenolysis of dodecanol to C11 hydrocarbon because methanol was formed during the reaction. On the other hand, dodecanol could be dehydrated to dodecene on the Brønsted acid site followed by the hydrogenation on the metal site. In the order of Ni/SiO_2 , $\text{Ni}_2\text{P}/\text{SiO}_2$ and MoP/SiO_2 , the decrease of the C11/C12 ratio reflects the decrease of the dehydrogenation/decarbonylation activity and the increase of the Brønsted acidity.

4.3.3. Formation of alkene and iso-alkane

In the deoxygenation of methyl laurate, n-alkanes were the main hydrocarbon products on Ni/SiO_2 and the Ni and Co phosphide catalysts. Apart from n-alkanes, alkenes and isoalkanes were also formed on MoP/SiO_2 , WP/SiO_2 , $\text{Fe}_2\text{P}-\text{FeP}/\text{SiO}_2$ and PO_x/SiO_2 . In the deoxygenations of lauric acid, dodecanal and dodecanol, alkenes and isoalkanes were also produced on MoP/SiO_2 and PO_x/SiO_2 , while they were trace on Ni/SiO_2 and $\text{Ni}_2\text{P}/\text{SiO}_2$.

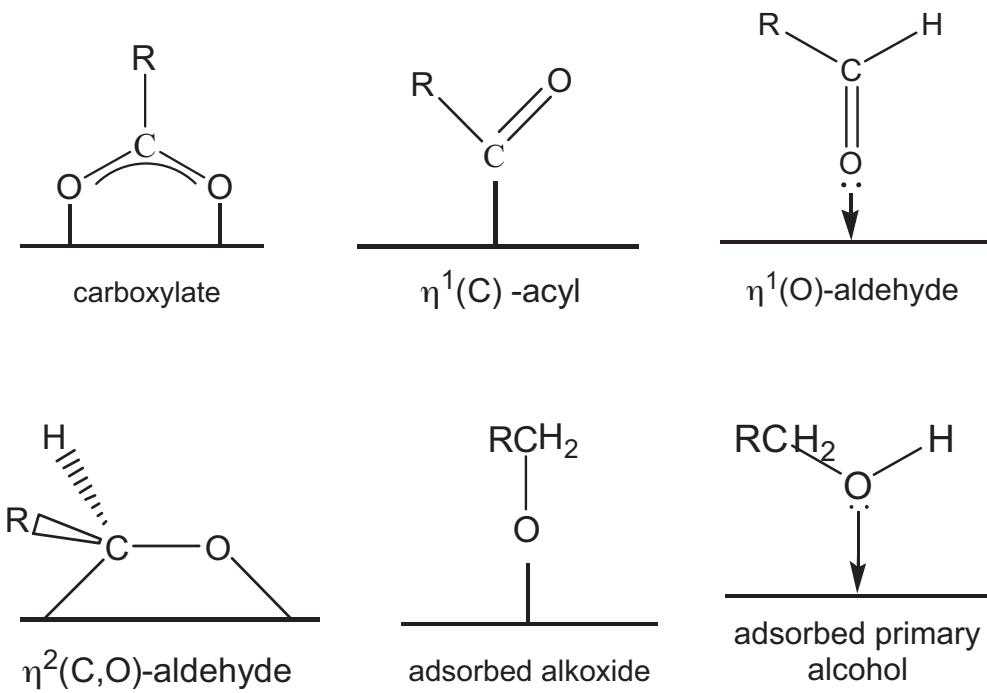


Fig. 10. Important oxygenate intermediates observed on transition metal surfaces [63].

During the deoxygenation of carboxyl acid or ester, alkenes can be produced via both decarbonylation and HDO pathways [78]. Of course, the dehydrogenation of alkane to form alkene cannot be excluded. Afterwards, alkene is either hydrogenated to alkane or combined H^+ to form carbocation intermediate [79]. The selectivity to alkenes is influenced by the catalyst property and the reaction condition [78,80,81]. Reducing hydrogenating ability of the catalysts increases the selectivity to alkenes [80]. The formation of alkenes on MoP/SiO₂, WP/SiO₂ and Fe₂P-FeP/SiO₂ may be ascribed to their lower hydrogenation abilities in comparison with those of Ni and Co phosphide catalysts. The hydrogenation ability is also related to the catalyst electron property. The high electron density of metal site favors the H_2 dissociation to form reactive hydrogen species required for hydrogenation [82]. It has been reported that the activity for the hydrogenation of benzene follows the order: Ni/SiO₂ > Ni₂P/SiO₂ > MoP/SiO₂ [27]. The formed alkenes combine with H^+ to produce carbocation intermediate followed by isomerization [79]. The formation of the isomerization products on Mo, W and Fe phosphide catalysts are mainly ascribed to the Brønsted acidity. In addition, the carbocation intermediate also underwent cracking to form light hydrocarbons, especially at high reaction temperature.

4.3.4. Formation of cracked hydrocarbons

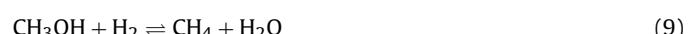
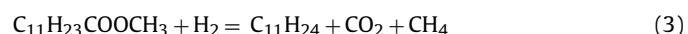
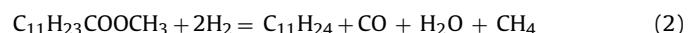
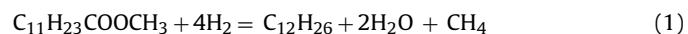
Compared to the nickel phosphide catalysts, Ni/SiO₂ showed much higher cracking activity. The nickel catalysts were also found to have higher cracking activities than the noble metal catalysts [14]. As the temperature increased, the selectivity to cracked products on Ni/SiO₂ was enhanced (see Fig. 3S in Supplementary material), whereas it did not change obviously (less than 1%) on Ni₂P/SiO₂ (Table 4). Therefore, Ni₂P/SiO₂ is in nature less active than Ni/SiO₂ for the cracking of C–C bond. This is mostly ascribed to the ligand and ensemble effects of P as previously discussed [20].

Different from Ni₂P/SiO₂, MoP/SiO₂ gave the increased selectivity to the cracked products as the reaction temperature increased. This should be ascribed to its lower hydrogenation ability and more Brønsted acidity, giving rise to forming the carbocation intermediates. The carbocation intermediates underwent cracking

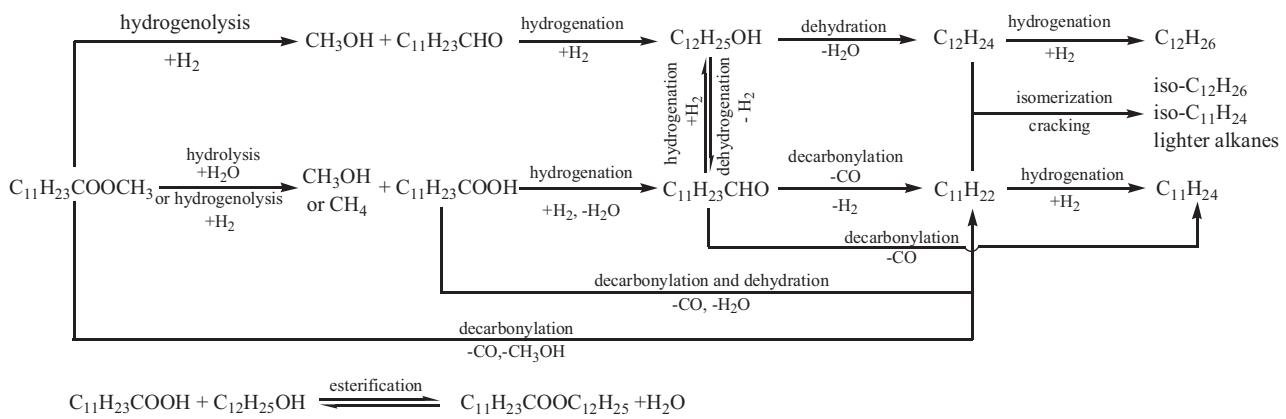
reaction, especially at high temperature. The cracking mechanism on MoP/SiO₂ is different from that on Ni/SiO₂.

4.3.5. CO/CH₄ ratio and H₂ consumption

From the industrial point of view, it is desired to reduce the H₂ consumption during the deoxygenation. As shown in the reactions (1)–(3), the decarbonylation/decarboxylation pathway consumes less H₂ but gives lower carbon yield than the HDO one. The methanation of CO or CO₂ (reaction (4) and (5)) should be avoided because it consumes more H₂. In addition, the water-gas shift reaction (6) can also occur. The reactions of CO, CO₂, H₂ and H₂O on catalyst surface are complex, while the gaseous composition can provide some valuable information about the deoxygenation mechanism and H₂ consumption.



In the deoxygenation of methyl laurate, both CO and CH₄ were formed on the metal phosphide catalysts, while CO was trace and CH₄ was predominantly produced on Ni/SiO₂. Actually, the nickel catalysts are very active for methanation. CO₂ was scarcely detected in the gaseous products for the phosphide catalysts. One case is that



Scheme 1. Proposed reaction pathway for deoxygenation of methyl laurate.

Table 9
CO₂ or CO hydrogenation on Ni₂P/SiO₂.^a

Reactants	Molar ratio of gaseous components	
	573 K	613 K
CO ₂ + H ₂	CO:CO ₂ = 0.028:1	CO:CH ₄ :CO ₂ = 0.057:0.004:1
CO + H ₂	CH ₄ :CO = 0.002:1	CH ₄ :CO = 0.016:1

^a Reaction conditions: 2.0 MPa, H₂/CO or H₂/CO₂ molar ratio = 25, gaseous hourly space velocity $1.41 \times 10^4 \text{ ml g}^{-1} \text{ h}^{-1}$.

the decarbonylation of methyl laurate did not take place. Another case is that CO₂ was converted to CO via reverse water-gas shift reaction. Our experiment result supports the former. As shown in Table 9, the conversion of CO₂ to CO or CO to CH₄ was very difficult on Ni₂P/SiO₂ even at 613 K. Therefore, it can be speculated that only decarbonylation took place on the metal phosphide catalysts in the deoxygenations of methyl laurate and its intermediates. As discussed below, the CO/CH₄ ratio can reflect the H₂ consumption.

In the deoxygenation of methyl laurate, Ni, Co and Fe phosphide catalysts gave the CO/CH₄ ratios larger than 1.0, while MoP/SiO₂ and WP/SiO₂ gave the CO/CH₄ ratios much less than 1.0. As indicated by the reactions (1)–(3) and (6), if there were no methanation reaction and hydrogenolysis/hydrolysis of ester group to form methanol (reactions (7) and (8)), the CO/CH₄ ratio would be 1.0, between 0–1.0 and 0 when there were only decarbonylation pathway, both decarbonylation and HDO pathways and only HDO pathway, respectively. Actually, methanol was formed probably via reactions (7) and/or (8). The formation of methanol reduced that of CH₄ and so increased the CO/CH₄ ratio. CO methanation and CH₃OH hydrogenation (reaction(9)) can produce CH₄ and consume H₂. However, the methanation scarcely occurred on the phosphides. Therefore, the larger the CO/CH₄ ratio was, the less H₂ consumption. If the catalyst gives more predominant decarbonylation pathway and less activity for methanol hydrogenation and methanation, it will give higher CO/CH₄ ratio. The Ni, Co and Fe phosphide catalysts gave the CO/CH₄ ratio larger than 1.0 because of the dominating decarbonylation pathway and the formation of CH₃OH. The predominant HDO pathway led to the CO/CH₄ ratio much smaller than 1.0 on MoP/SiO₂ and WP/SiO₂. Additionally, as the temperature increased or the WHSV decreased, the CO/CH₄ ratio decreased. Since the amount of CO is close to that of C11, the decrease of CO/CH₄ ratio indicates that the methanol hydrogenation and/or the hydrogenolysis of O-CH₃ bond were promoted.

In contrast to Ni/SiO₂, the nickel phosphide catalysts were much less active for the methanation. This should be ascribed to the “ligand” and “ensemble” effects of P[20], which reduces the interaction between Ni₂P and CO/H₂ and hampers CO/H₂ adsorption [55,56].

4.4. Summary on deoxygenation mechanism and roles of metal and acid sites

Two deoxygenation pathways (i.e., HDO and decarbonylation) occurred on the phosphides in the conversion of methyl laurate. As indicated in Scheme 1, a series of reactions took place during the reaction. They include hydrogenolysis, hydrolysis, hydrogenation, decarbonylation, dehydrogenation, dehydration, esterification, isomerization, cracking as well as polymerization.

First, methyl laurate can be converted to: (1) lauric acid via hydrogenolysis or via hydrolysis; (2) dodecanal via hydrogenolysis; (3) undecene via decarbonylation. Lauric acid and dodecanal may be the primary intermediates because lauric acid was the main intermediate and methanol was produced. Lauric acid can further be converted to dodecanal via hydrogenation or undecene via decarbonylation. For the HDO pathway, dodecanal is easily hydrogenated to produce dodecanol. Dodecanol is then dehydrated to form dodecene or adversely dehydrogenated to form dodecanal. Dodecene is either hydrogenated to dodecane or transformed to carbocation on Brønsted acid site followed by isomerization and hydrogenation to produce isododecane or cracking reaction. For the decarbonylation pathway, dodecanal is converted to undecane or undecene via decarbonylation/dehydrogenation. Undecene can be converted with the same pathways to dodecene, yielding undecane, isoundecane and cracked hydrocarbons.

Although hydrogenolysis, decarbonylation and hydrogenation occurred on the P-OH group (i.e., Brønsted acid site), they were mainly catalyzed by the metal site. The metal site with higher electron density gave the higher activities for decarbonylation and hydrogenation, giving rise to the larger C11/C12 ratio and less amount of alkenes. Also, there might be a synergism between the metal and Brønsted acid site for the conversion of methyl laurate. Brønsted acidity also catalyzed the other reactions: the hydrolysis of methyl laurate to form lauric acid; the dehydration of dodecanol to dodecene; the esterification of lauric acid with dodecanol to form dodecyl laurate; the isomerizations of dodecene and undecene by forming carbocation intermediates, whereas the carbocations were alternatively transformed to lighter alkanes via cracking reaction; the polymerization.

The polymerization reactions (such as aldol condensation, olefin polymerization and ketonization of carboxylate species) could occur on acid site as well as the oxygen vacancy [83–85], giving rise to heavy products. This is indicated by the colors (yellow or brown) of liquid products for PO_x/SiO₂. Specially, in the conversion of dodecanal on PO_x/SiO₂, there was a great deal of brown insoluble substance in the liquid product. In addition, the fresh PO_x/SiO₂ was white, whereas the used PO_x/SiO₂ was brown or black, indicating that there was carbon deposition. Because the heavy compound

could not elute from GC, the total selectivity to the detectable products was different to 100% for PO_x/SiO_2 . The hydrogenation ability of the metal phosphide catalysts inhibited the formation of heavy compounds. Moreover, the higher the catalyst activity was, the less the deviation.

5. Conclusion

Under the condition of 573 K, 2.0 MPa, WHSV of 5.2 h⁻¹ and $\text{H}_2/\text{methyl laurate}$ ratio of 25, the conversion of methyl laurate followed the sequence: $\text{Ni}_2\text{P} > \text{MoP} > \text{CoP}-\text{Co}_2\text{P} > \text{WP} > \text{Fe}_2\text{P}-\text{FeP}_2; \text{Ni} \approx \text{Ni}_2\text{P} > \text{Ni}_{12}\text{P}_5 > \text{Ni}_3\text{P}$. The catalyst activity is related to the surface metal site density, the electron density of metal site and the Brönsted acidity. There might also be a synergism between the metal and Brönsted acid site. The nickel phosphide catalysts consumed much less H_2 than metallic Ni due to lower activities for methanation and cracking reaction.

In the deoxygenation of methyl laurate, Ni, Co and Fe phosphides mainly gave the decarbonylation hydrocarbons, whereas MoP and WP dominantly yielded the HDO hydrocarbons. In the order of Ni, Ni_3P , Ni_{12}P_5 and Ni_2P , the selectivity between the decarbonylation and HDO pathways tended to decrease. The decarbonylation pathway is promoted by increasing the electron density of metal site. Metallic Ni, Ni and Co phosphides primarily gave n-alkanes. Fe, Mo and W phosphides also yielded alkenes and isohydrocarbons apart from n-alkanes, which is ascribed to their low hydrogenation ability and high Brönsted acidity. Increasing temperature and decreasing WHSV enhanced the conversion of methyl laurate and the C11/C12 ratio. With increasing temperature, the selectivity to cracked products did not obviously change on Ni_2P , whereas it increased on MoP due to the mechanism associated with carbocation. In all, the deoxygenation mechanism is mainly affected by the electron structure of metal site and Brönsted acidity.

In the deoxygenations of lauric acid, dodecanal and dodecanol, Ni/SiO_2 also gave the dominating decarbonylation product and high selectivity to the cracked products, while MoP/SiO_2 still mainly yielded the HDO product. $\text{Ni}_2\text{P}/\text{SiO}_2$ gave lower C11/C12 ratios in the deoxygenations of dodecanal and dodecanol than those in the deoxygenations of methyl laurate and lauric acid. The C11/C12 ratio on PO_x/SiO_2 was larger than 1.0 in the conversions of methyl laurate and lauric acid, whereas it was much lower than 1.0 in the conversions of dodecanal and dodecanol. The deoxygenation pathway is related not only to the catalyst property but also to the kind of reactant.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2013.08.026>.

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